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PROVISIONAL SPECIFICATION

Applicants:

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION

-and-

UNIVERSITY OF WOLLONGONG

Invention Title:

ELECTROCONDUCTIVE TEXTILES

The invention is described in the following statement:

ELECTROCONDUCTIVE TEXTILES

FIELD OF THE INVENTION

The present invention relates to electroconductive textiles and methods for producing electroconductive textiles.

BACKGROUND OF THE INVENTION

It has been recognized for some time that the electrical properties of inherently conductive polymers (ICPs) can best be exploited by their incorporation into host structures that provide the required mechanical and physical properties for a given application. Textiles produced from naturally occurring and synthetic fibres are particularly suited to this purpose.

Inherently conductive polymers immobilised by a textile substrate could be used for a number of applications. These electroconductive textiles can be used in the production of clothing articles which function as wearable strain gauges for use in biomechanical monitoring, or direct biofeedback devices for sports training and rehabilitation. In these articles physical changes in the textile cause changes to electrical resistance or electrical conductivity which can then be monitored. Other applications include the production of clothing articles which change their thermal insulation or moisture transport characteristics in response to changing climatic conditions. Electroconductive textiles can also be used in applications where antistatic or EMI shielding properties are required. A further application is for use in heating devices such as car seats, car seat covers and gloves.

Currently known textile materials coated with

inherently conductive polymers suffer from a number of disadvantages.

Ideally, electroconductive textiles should contain electronic components seamlessly integrated into the conventional textile structure, exhibit stable electrical properties, withstand normal wear, and be launderable. There are currently no commercially available conducting polymer coated textiles that fulfil all of these requirements. It would also be desirable for conventional textile dyeing or printing techniques to be used in the production of the electroconductive textile, however this is usually not possible due to the poor solubility properties of the inherently conductive polymers and some monomer precursors in water.

One current method used for preparing electroconductive textiles involves *in situ* polymerisation of the inherently conducting polymer onto a substantially non-conductive textile substrate. However, there is no apparent bonding between the non-conductive textile and the inherently conductive polymer (including some monomer precursors from which the polymer is formed). Consequently, the polymers can be easily abraded or displaced from the textile, or during laundering the textile may suffer from rapid loss of conductivity. In addition, the polymer component of the electroconductive textile can easily change oxidation state or be dedoped. Moreover, the polymer coating containing the conductive material can significantly change the properties of the non-conductive textile to which it is applied.

For similar reasons, the use of curing agents to affix conductive polymers onto the surface of textile substrates is also disadvantageous.

Another technique currently used for the

production of an electroconductive textile involves making the textile fibres from the conductive polymer itself and forming a fabric from the fibres. However, the nature of conductive polymers is such that the fibres are relatively brittle and inextensible and textiles formed from these fibres also suffer from these limitations. In addition, since the conductive polymer component of an electroconductive textile is much more expensive than non-conductive textiles such as cotton, wool and nylon, the electroconductive textile produced by this method is prohibitively expensive.

Another technique explored more recently has involved the polymerisation of conducting polymers onto the chemically activated surface of a textile material. This requires actual pre-functionalisation of the textile material to create a chemically activated textile which will ionically bond with the conductive polymer. As one example, a non-conductive textile made from a suitable material (for example, polyethylene) is subjected to phosphonylation and then the conductive polymer is polymerised onto the phosphonylated textile. Although this gives rise to a strong bond between the textile and the inherently conductive polymer, this requires modification of the non-conductive textile, which may alter its desirable properties as a textile.

The existing methods also suffer from the fact that there are limited means besides altering the level of doping to control the conductivity of the electroconductive textile.

Another problem associated with the current systems for producing electroconductive textiles relates to the nature of the inherently conductive polymers themselves. A large proportion of known inherently conductive polymers are insoluble in solvents,

particularly water. This makes it very difficult to bring the conductive polymers into intimate contact with the textile.

Accordingly, it is an object of the present invention to provide a new approach for the production of electroconductive textiles that address these problems.

SUMMARY OF INVENTION

According to the present invention there is provided an electroconductive textile comprising:

- a non-conductive textile,
- a macromolecular template which is bonded to or entrapped in the non-conductive textile, and
- a conductive polymer which is ordered by and bonded to the macromolecular template;

such that the macromolecular template binds the conductive polymer to the non-conductive textile.

By using a molecular template of a type that is capable of directly binding to or being directly entrapped within the non-conductive textile (i.e. not by affixing with an interposed curing agent), a number of advantages are achieved. Firstly, the macromolecular template will improve the conductive nature of the conductive polymer by inducing order in the conductive polymer. In addition, the macromolecular template and the reaction conditions for directly coupling the macromolecular template to the conductive polymer can be chosen to control the level of conductivity of the conductive polymer.

Another advantage of using a macromolecular template is that a suitable preformed templated conducting polymer can be prepared that will make the conductive polymer soluble in the desired solvent, so as to facilitate the bringing of the conductive polymer into

contact with the non-conductive textile. Similarly, a mixture of the macromolecular template with the subunits from which the conducting polymer is made enables solubilization of the subunits in the desired solvent so as to facilitate the bringing of the conductive polymer into contact with the non-conductive textile. This allows for conducting polymers to be applied to textiles using techniques that were otherwise not possible, and without the need for a curing step to bind the conducting polymer to the textile. Various other advantages associated with the use of the molecular template will be explained in further detail below.

According to the present invention there is also provided a method for preparing an electroconductive textile from a non-conductive textile and polymer subunits which, when polymerised, form a conductive polymer, the method comprising the steps of:

(i) polymerising the polymer subunits in the presence of a macromolecular template to form the conductive polymer bound to the macromolecular template; and

(ii) contacting the macromolecular template with the non-conductive textile to effect bonding of the molecular template to the non-conductive textile.

As will be explained in further detail below with reference to the main alternative techniques for preparing the electroconductive textile, step (ii) outlined above can be conducted prior to, or following step (i). Consequently, the applicant envisages three main methods by which the electroconductive textile can be prepared.

The first alternative method for preparing the electroconductive textile comprises the steps of:

(a) contacting the macromolecular template with the non-conductive textile to effect bonding of the

macromolecular template to the non-conductive textile, and

(b) contacting the polymer subunits with the macromolecular template bound to the non-conductive textile, and polymerising the polymer subunits to form the conductive polymer bound to the macromolecular template and to the non-conductive textile via the macromolecular template.

The second alternative method for preparing the electroconductive textile comprises the steps of:

(a) contacting the non-conductive textile, the macromolecular template and the polymer subunits with one another to effect bonding of the macromolecular template to the non-conductive textile, and bonding of the macromolecular template to the polymer subunits, and

(b) polymerising the polymer subunits to form the conductive polymer which is bound to the non-conductive textile via the macromolecular template.

The third alternative method for preparing the electroconductive textile comprises the steps of:

(a) contacting the macromolecular template with the polymer subunits and polymerising the polymer subunits to form the conductive polymer bound to the macromolecular template, and

(b) contacting the macromolecular template with the non-conductive textile to effect bonding of the macromolecular template to the non-conductive textile, with the conductive polymer bound to the non-conductive textile via the macromolecular template.

According to the present invention there is also provided a new use of a macromolecular template having properties which makes it capable of binding with a non-conductive textile, in the preparation of an electroconductive textile from the non-conductive textile and polymer subunits which, when polymerised, form a

conductive polymer.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is described further by way of example with reference to the accompanying drawings in which:

Figure 1 illustrates schematically the three main techniques for forming the electroconductive textile of the present invention; and

Figure 2 is a UV/VIS Spectrum of PMAS and templated PMAS/PAn treated wool/nylon/Lycra.

DETAILED DESCRIPTION OF THE INVENTION

As explained above, there are three main techniques for forming the electroconductive textile of the present invention. These are schematically illustrated in Figure 1.

The first alternative method represented by (I) involves applying the macromolecular template represented by A to the textile, represented by T. In a second step the polymer sub-units represented by B are brought into contact with the macromolecular template A bound to the non-conductive textile T, and polymerisation is effected while *in situ* in the textile to produce the electroconductive polymer C. The final product, which may need to be subjected to further treatment steps such as doping, is the electroconductive textile X.

The second alternative method for preparing the electroconductive textile X is represented by (II). According to this method, the macromolecular template A is contacted with the polymer subunits B, prior to or at the

same time that it is contacted with the textile T. This will yield a treated non-conducting textile containing the macromolecular template and polymer subunits. In a second stage, polymerisation of the subunits B is effected to produce the electroconductive polymer C and thus yield the electroconductive textile X.

The third alternative method for preparing the electroconductive textile X is represented by (III). According to this method, the macromolecular template A is brought into contact with the polymer subunits B, which are then polymerised to yield a preformed templated conductive polymer as represented by Y. The preformed templated polymer Y is then applied to the textile to yield the electroconductive textile X.

In the following we have explained the meaning of the various terms used in the specification for complete understanding of the scope of the invention.

Non-conductive Textile Material

The term "textile material" or "textile" is used herein in its broadest sense and includes yarns, threads, fibres, cords, filaments, fabrics, cloths and materials that have been woven, knitted, felted, thermally bonded, hydroentangled, spunbonded, meltblown, electrospun or formed from other nonwoven processes or formed from the foregoing, and combinations thereof.

The term "non-conductive" means that the textile material is non-conductive, or has very low conductivity. Non-conductive is defined as having a surface resistivity of greater than 10^{11} Ω/square. The surface resistivity is measured according to ASTM standard method D-257 (Electrical Resistance of Insulating Materials).

The textile material may be formed from natural or synthetic fibres or a combination of the two. Natural fibres include, notably, cellulosic fibres and proteinaceous fibres, such as cotton, hemp and wool. Synthetic fibres include the range of polymers that have been made in a fibre form, including polyalkylenes (and homopolymers or copolymers; examples of the homopolymers being polyacrylonitrile and polypropylene); polyamides including nylon (such as nylon 6 and nylon 66), Kevlar® and Nomex®; polyurethanes, including polyurethane block copolymers (such as Lycra®); polyureas (and block copolymers thereof such as polyurethaneureas); polyesters such as polyethylene terepthalate (PET); and synthetic cellulose-derived fibres, such as rayon, and combinations thereof.

According to one embodiment, the non-conductive textile is a natural fibre-containing textile, suitably a wool-containing textile.

Preferably, the non-conductive textiles used in the present invention are not functionalised to enable a reaction creating an ionic bond to be formed between the textile and the macromolecular template. The ability for such textiles to be made into electroconductive textiles without functionalisation, by use of the claimed molecular templates, is an advantage of the present invention.

Similarly, the textiles can be made electroconductive by techniques that do not require a curing step to bind the conducting polymer to the textile. This is also an advantage of the present invention.

Conductive Polymer

The term "conductive polymer" is used broadly to refer to any of the class of conductive polymers known in

the art. These are sometimes referred to as "inherently conductive polymers".

Conductive polymers are unsaturated polymers containing delocalised electrons and an electrical charge. Conductive polymers may be positively or negatively charged (cationic or anionic), and are associated with counter ions referred to as the dopant. Polymers in the main class of conductive polymers are polymerised from their polymer subunits by oxidation. These will be referred to as the oxidatively polymerised conductive polymers.

The term conductive polymer is used in its broadest sense to refer to doped and dedoped conductive polymers, and therefore it encompasses any of the polymers which form polaronic (including bipolaronic) moieties. Generally, polarons are the charge carrying species which are generated by the oxidation of the conjugated polymer backbone.

Examples of suitable conductive polymers are polypyrrole and its derivatives, polythiophene and its derivatives, phenyl mercaptan and its derivatives, and polyaniline and its derivatives, or combinations thereof. Suitable derivatives are those that contain functional groups, such as a methoxy group. Examples within the range of other optional functional groups are alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, aryloxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, amino,

alkylamino, dialkylamino, alkenylamino, alkynylamino, arylamino, diarylamino, benzylamino, dibenzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, diacylamino, acyloxy, alkylsulphonyloxy, arylsulphenyloxy, heterocyclyl, heterocycloxy, heterocyclamino, haloheterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, benzylthio, acylthio, sulphonate, carboxylate, phosphonate and nitrate groups or combinations thereof. The hydrocarbon groups referred to in the above list are preferably 10 carbon atoms or less in length, and can be straight chained, branched or cyclic.

Dopant

Dopants or doping agents provide the counter ions which are associated with the conductive polymers. These may be derived from strong acids such as p-toluene sulphonic acid, naphthalene disulphonic acid, methane sulphonic acid, chloromethyl sulphonic acid, fluoromethyl sulphonic acid, oxalic acid, sulphosalicylic acid and trifluoroacetic acid. However, as explained below, the dopant may be provided by the macromolecular template or another agent (for example, the acid moiety of the functional groups present in any reagent used in forming the electroconductive textile). Oxidizing agents such as ammonium persulphate, ammonium peroxydisulphate, ferric chloride, salts of permanganates, peracetates, chromates and dichromates may contribute to the doping effect.

Polymer Sub-units

The term "polymer sub-unit" is used herein to refer to monomers, dimers, multimers (eg oligomers) and mixtures thereof that, upon polymerisation, form a

polymer. In the context, the polymer formed may be a conductive polymer. The polymer subunits which form the conductive polymer may be the same or different. Furthermore, the dimer and multimer may be formed from monomer units which are the same or different. Consequently, the conductive polymer may be a homopolymer or a copolymer.

Examples of suitable polymer sub-units are aniline, thiophene, bithiophene, terthiophene, pyrrole, phenyl mercaptan, indole, carbazole, acrylate, and derivatives thereof. Pyrrole, thiophene and aniline and their derivatives are particularly preferred.

Polymer

The term polymer is used in its broadest sense to encompass homopolymers, copolymers, oligomers and so forth, unless the context is to the contrary.

Macromolecular template

The term "molecular template" refers to any chemical, compound or substance that provides a template upon which, or in relation to which, the polymer subunits of the conductive polymer will preferentially align to induce the desired orientation of the subunits for forming the conductive polymer. For instance, where the polymer is to be preferentially para-directed during synthesis, an appropriate template is one, which causes the polymer subunits to be aligned to form a complex with the template that leads to mostly para-directed synthesis, with limited alternative branching. The prefix "macro" means that the molecular template is a macromolecule in size. Macromolecule is defined as a molecule of high relative

molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass. Generally, macromolecules have a molecular weight of about 1000 or more, suitably 1200 or more. The term "macromolecular template" encompasses polymeric molecular templates, and indeed particular embodiments of the invention utilise polymeric molecular templates.

Although a large range of substances are known to function as molecular templates, it is noted that the macromolecular templates of the present invention must be compounds that are capable of bonding with or being entrapped within the non-conductive textile. Consequently, not all materials described in the prior art as molecular templates function as macromolecular templates as defined in the present application.

The templates of the present invention are "molecular" in that they provide template-guiding on a molecular level, rather than a physical level.

The macromolecular templates provide strands along which the polymer subunits that form the conductive polymer can be bound in an ordered fashion by non-covalent intermolecular interactions to form a stable molecular complex.

The macromolecular templates may be non-conductive or conductive. The use of conductive macromolecular templates is of particular interest, as they can add to the conductive properties of the

electroconductive textile themselves.

Electrically conductive macromolecular templates, and particularly polymeric molecular templates, encompass conductive polymers containing one or more acid, ester or salt (electrolyte) groups, and derivatives thereof. The acid or ester group is one that contains a carbon, sulphur, nitrogen or phosphorous to oxygen double bond, and a single bond from said carbon, sulphur, nitrogen or phosphorous atom to another oxygen (or sulphur or nitrogen) atom. Accordingly, this class of functional groups includes sulphates, sulphonates, carboxylates, phosphonates, nitrates, amides, and the acid equivalents (such as sulphonic acid, carboxylic acid, and so forth) and derivatives thereof. Sulphonate and sulphate groups are preferred. Such conductive macromolecular templates containing sulphonate and/or sulphate may be fully or partially sulphonated.

These conductive polymers may contain any other functional groups, such as a methoxy group. Examples within the range of other optional functional groups are alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, aryloxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, amino, alkylamino, dialkylamino, alkenylamino, alkynylamino, arylamino, diarylamino, benzylamino, dibenzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, diacylamino, acyloxy, alkylsulphonyloxy, arylsulphenyloxy, heterocyclyl, heterocycloxy, heterocyclamino, haloheterocyclyl, alkylsulphenyl,

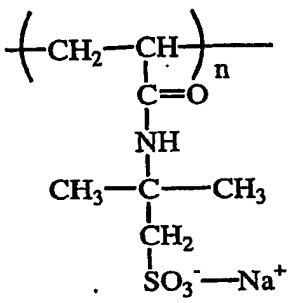
arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, benzylthio and acylthio. The hydrocarbon groups referred to in the above list are preferably 10 carbon atoms or less in length, and can be straight chained, branched or cyclic.

A preferred class of conductive macromolecular templates encompasses the sulfonated polyanilines, sulfated polypyrroles, and sulfonated polythiophenes, and derivatives thereof. One particularly useful molecular template within this class is poly 2-methoxyaniline-5-sulfonic acid (PMAS).

Examples of non-conductive macromolecular templates which can be used are polyvinylsulfonate, polystyrene sulfonates, biologically active polymers such as heparin, chondroitin sulfate and dextran sulfate, as well as large multicharged ions such as calixarenes, cyclodextrins and selected polymeric textile dyestuffs. Although these compounds are non-conductive, they can provide dual functions. For instance, these compounds function as molecular templates, and may also function as a dopant or dye for colouring of the textile.

Thermally sensitive polyelectrolytes such as poly-2-acrylamido-2-methyl propane sulfonic acid (PAMPS) (Formula I) and co-polymers comprising the AMPS monomer (Formula II) are other examples of macromolecular templates which can be used. Variations in the composition can be used to tune the temperature at which the polyelectrolyte collapses (becomes less soluble). Indeed, this change in conformation of the polyelectrolyte

influences the conductivity of the templated conductive polymer



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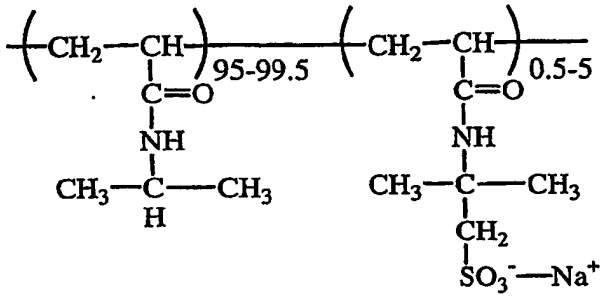


(II)

Redox containing polyelectrolytes such as polyvinyl ferrocene sulfonate are other examples of macromolecular templates that provide a function in addition to the molecular template function. Other classes of macromolecular templates that provide a dual function comprise UV absorbers, fluorescent whitening agents, stain blocking agents and shrinkproofing polymers which are also macromolecular templates. It is to be noted, however, that not all UV absorbers, fluorescent whitening agents, stain blocking agents and shrinkproofing polymers are or can act as macromolecular templates.

As mentioned above, the macromolecular template may be conductive, and in this instance the molecular template can be either a cationic or anionic conductor. Cationic macromolecular templates may be used to bind an anionic conductive polymer to the non-conductive textile. Similarly, an anionic macromolecular template may be used to bind a cationic conductive polymer to the non-conductive textile.

Polyelectrolytic molecular templates are the preferred class of macromolecular templates, and an example includes PMAS.

In a preferred embodiment, the macromolecular template can provide an environment for facile oxidation of the polymer subunits to form the conductive polymer.

Bound

The term "bound" or "bonded" or "bind" refers to non-covalent or covalent intermolecular interactions between two compounds. Hydrogen bonding is encompassed by this term. This term is used in the sense of direct bonding between two compounds without an interposed agent such as a curable adhesive. Covalent bonding refers to the direct interaction between the macromolecular template and the textile, or the macromolecular template and the conducting polymer. Non-covalent bonding encompasses ionic intermolecular interactions sufficient to bond one surface directly to the other without any interposed agent such as an adhesive.

One test for determining whether the conductive polymer is bound to the non-conductive textile via the macromolecular template only as required herein involves subjecting the product to sonication to detect evidence of loss of the conductive polymer from the textile. Removal of conductive polymer during the sonication test indicates that the conductive polymer is not bound by the intermolecular interactions. Another simple test correlates to the standard test used in fabric dyeing to determine whether a colouring agent has bonded to the

fabric or not. This involves rubbing the textile against white fabric. Marking of the white fabric demonstrates that the dye has not bonded to the fabric.

In the non-printing methods for applying the conductive polymer to the non-conductive textile, the mechanism of binding is preferably not a curing mechanism.

Entrapment

The expression "entrapped in" refers to the situation where the macromolecular template forms an interpenetrating network through the textile fibre matrix. The expression "interpenetrating network" is well understood in the field of polymers and is used in the same sense here. It involves the polymer chains extending into the textile fibre matrix and being entrapped therein without direct covalent chemical bonding.

Polymerisation

The polymer sub-units are polymerised by any process appropriate for the particular monomers involved. This encompasses addition polymerisation or condensation polymerisation, with free radical initiation, where required, produced by redox reaction, light or microwave. Usually the polymerisation is by way of addition polymerisation for the production of the conductive polymer.

The contacting of the various components with one another in the methods of the invention can be achieved by any appropriate technique. Advantageously this is achieved by one of the conventional textile dyeing techniques, including padding, exhaustion, printing and

coating including foam applications.

Products made from electroconductive textiles

The electro-conductive textiles of the present invention may be used to manufacture articles requiring electroconductive properties. The articles may be made partly or entirely from the electroconductive textile. Examples include gloves, car seats, heating panels for car seats, protective clothing, hosiery, and other apparel items, footwear, headgear, strain gauges, energy storage devices such as batteries or capacitors, and energy conversion devices.

The present invention provides additional functionality, and overcomes compatibility issues of some conductive polymers with non-conductive textiles when the prior art is employed. The present invention also provides a means of locating the conductive polymer either inside the non-conductive textile or on its surface, thereby allowing users to further tailor electroconductive textiles to suit individual applications and requirements.

Other Product and Process Options

As indicated above, the macromolecular template can itself be a conductive polymer. In this situation, the electroconductive textile comprises a non-conductive textile, having a conductive macromolecular template bonded thereto, and a conductive polymer (which may be the same substance or a different substance to the macromolecular template) bonded thereto. It is also possible, according to this embodiment or any other embodiment, to apply to the 3 component electroconductive textile one or more further layers of conductive polymer.

EXAMPLES

A number of preferred embodiments are described by reference to the following non-limiting examples.

Most of the examples provided below utilise poly 2-methoxyaniline-5-sulfonic acid (PMAS) as the macromolecular template. This macromolecular template is itself a conductive polymer, and therefore some conductivities are reported for textiles to which the macromolecular template has been applied. However, to avoid misunderstanding, it is noted that not all conductive polymers are capable of functioning as a macromolecular templates which both provide the templating function for the conductive polymer, and bond to a non-conductive textile. Nevertheless, as these precursors in the preparation of the electroconductive textiles of the present invention do have conductive properties, their levels of conductivity have been reported on occasion in the following examples.

Furthermore, in the examples, the % exhaustion (for example, of molecular template onto non-conductive textile) was determined from UV/VIS absorption spectroscopy. For PMAS, this was calculated from the 474nm absorption peak. The measurements were taken at the end of the process step (eg after 4 hours and 30 minutes application time). This is confirmed in the Tables where * is marked.

For electrical resistance, the values reported represent the mean and standard deviation of 3 readings on

a single textile treatment. Measurements were determined on a standard sample size of 4cm x 4cm across a 1.5cm path length. This is confirmed in the Tables where # is marked.

1. FIRST ALTERNATIVE METHOD FOR FORMING ELECTROCONDUCTIVE TEXTILE

1.1 Step 1: Application of Macromolecular Template to Non-Conductive Textile

In this section we demonstrate methods for applying the macromolecular template of the preferred embodiment of the invention to a non-conductive textile. Whilst this corresponds directly to the first step of the first alternative method for forming the electroconductive textile of the invention, the same techniques apply to any of the steps of the second and third alternative methods (illustrated in Figure 1) in which a macromolecular template is contacted with the non-conductive textile, irrespective of whether or not the macromolecular template has already been contacted with the polymer subunits.

1.1.1 Exhaust Application of PMAS onto Wool-based Textiles

PMAS (10% on mass of fabric (omf)) was applied to a scoured chlorine-Hercosett treated wool knit textile using an Ahiba Texomat Laboratory Dyeing Machine with the wool textile being wound onto a spindle and submerged in the application liquor. A liquor:goods ratio of 50:1 was used and the PMAS application was made to 2g sample of textile which had been wet prior to use by soaking at room temperature for 10 minutes in 1g/L Lissapol TN450 (ICI,

non-ionic surfactant) followed by a distilled water rinse and a final 10 min soak in acid solution at the desired pH.

The PMAS solution was adjusted to pH 1.40 by the drop-wise addition of 10% w/v H_2SO_4 to the stirred solution. The wool textile was introduced to the application bath at 40ºC, heated to 90ºC over 30 minutes, and the temperature maintained for a further 4 hours. The textile sample was then removed from the application liquor and rinsed in cold tap water until no signs of 'bleed" were evident. Excess water was removed and the sample was air-dried at room temperature overnight prior to measurement of the electrical resistance.

This basic process was used for the application of the macromolecular template to the non-conductive textile unless otherwise stated.

1.1.2 Variation of Application pH

The process outlined in 1.1.1 above was repeated with modification of the initial pH of the PMAS application liquor. The results of these trials are demonstrated in Table 1.

Table 1:

Initial pH	Final pH	Final % PMAS Exhaustion*	Textile Electrical Resistance$^{\theta}$
2.66	4.20	50.0	170 +/- 22 GΩ
1.99	2.45	52.7	3.1 +/- 0.1 GΩ
1.80	2.04	60.3	484 +/- 24 MΩ
1.60	1.77	71.5	125 +/- 11 MΩ
1.40	1.54	86.3	60 +/- 4 MΩ

These trials demonstrate that PMAS uptake is dependent upon the application pH. Lowering the initial pH results in increased uptake of the PMAS and decreased electrical resistance of the treated textile.

Non-conductive textiles other than wool can be subjected to an application pH of less than pH 1.4 due to better stability of the textile in acid at the process temperatures. Wool non-conductive textiles, however, are preferable treated at pH 1.4 or above. Under these conditions the wool textiles produced were structurally intact, with no obvious weakening of the textile integrity. The coated textiles could be stretched up to 70%, without tearing.

1.1.3 Variation in Application Temperature

The process outlined in 1.1.1 above was repeated with modification of the temperature of the PMAS application liquor. The results of these trials are set out in Table 2.

Table 2:

Appl. Temp. (°C)	Initial pH	Final pH	Final % PMAS Exhaustion*	Textile Electrical Resistance#
60	1.40	1.43	38.0	5.4 +/- 0.2 GΩ
70	1.40	1.42	38.7	911 +/- 20 MΩ
80	1.40	1.42	51.9	154 +/- 8 MΩ
90	1.40	1.54	86.3	60 +/- 4 MΩ
100	1.40	1.54	100.0	310 +/- 12 MΩ

Higher application temperatures are preferred for

maximising uptake of the macromolecular template, although ultimately the temperature used may be influenced by other factors such as electrical resistance and textile deterioration.

1.1.4 Variation in acid used to adjust pH

The standard method outlined in 1.1.1 for the uptake of PMAS on wool was repeated with the substitution of the sulphuric acid with other acids. The result of this trial is set out in Table 3.

Table 3:

Acid	Initial pH	Final pH	Final % PMAS Exhaustion*	Textile Electrical Resistance#
H_2SO_4	1.40	1.36+/- 0.01	96.8+/-1.2	85+/-5 MΩ
HCl	1:38	1.53+/- 0.2	99.9+/-0.2	1.5+/-1.2 GΩ
p-Toluene Sulfonic Acid	1.40	1.51	92.3	105+/-0.3MΩ
10-Camphor Sulfonic Acid	1.40	1.49	87.3	66+/-0.1MΩ

1.1.5 Variation in PMAS Concentration

The process outlined in 1.1.1 above was repeated with modification to the PMAS concentration, measured as a percentage based on the mass of the non-conductive textile. The results of these trials are set out in Table 4.

Table 4:

Initial		Final % PMAS	Textile Electrical

PMAS Conc. (% omf)[&]	Final pH	Exhaustion*	Resistance (MΩ)[#]
5	1.48	99.4	301 +/- 8
10	1.54	71.1	33.2 +/- 0.7
15	1.42	59.3	26.7 +/- 0.4
20	1.42	46.9	30.3 +/-0.4

[&] "omf" refers to "on the mass of fabric".

1.1.6 Variation of Macromolecular Template

The method outlined in 1.1.1 above was repeated with the replacement of the PMAS with a range of other macromolecular templates applied at 10% offer based on weight of fabric. The results of the exhaustion levels from this study, as determined by UV/VIS, are set out in Table 5 below:

Table 5

Molecular Template	% Exhaustion level
Basyntan D liquid (BASF)	80
Seicitan D Liquid (Seici)	76
Intan EMS (Alpa)	96
Trupotan R83 (Trumpler)	42
Synthaprett BAP (Bayer)	34
Orotan SN Powder (Bayer)	90
Poly (styrene sulfonic acid/maleic acid) (Polysciences Inc.) 3:1 or 1:1	75-80%

1.1.7 Variation of Non-Conductive Textile.

The process outlined under 1.1.1 above was repeated with the substitution of the wool textile

described there with the following textile composites:

wool/nylon/Lycra;
wool/polyester;
nylon;
nylon/Lycra; and
cotton.

3 different wool/nylon/Lycra fabrics were used. They ranged in wool content from 90-97%, nylon 2-8%, and Lycra 0.5-1%, and were of approximately 270g/m^2 density. These fabrics were manufactured by the applicant, and have commercially available equivalents.

The nylon and nylon/Lycra were commercially available textiles obtained from a retailer of fabrics. The cotton was a scoured fabric that again was knitted by the applicant, having similar properties to commercially available cotton fabric.

The wool-based templated textiles produced had similar electrical resistance to the 100% wool textiles reported in 1.1.1 above.

1.1.8 Other Application Techniques for PMAS

Examples 1.1.1 - 1.1.8 all relate to the application of the macromolecular template to the non-conductive textile by the exhaust technique, in which the non-conductive textile is saturated in an application liquid containing the macromolecular template. In the following we have exemplified other application techniques.

1.1.8.1 Padding

A pad liquor (100ml) was prepared containing 66.7g/l PMAS, 300g/l Urea and 2g/l Lissapol TN450 (non-ionic surfactant, ICI) at 20°C. The pH of the pad liquor prior to use was 2.87. A 5g sample of wool textile was added to the pad liquor, the fabric allowed to become saturated with the liquor over 2 minutes with mild agitation by hand, then withdrawn and passed through squeeze rollers set to control pickup to 150%. These conditions had the effect of applying 10% PMAS on the weight of textile. After this treatment, the sample was placed in an airtight plastic bag and "batched" at 60°C in a forced-air oven for 24 hours. Following this period, the sample was removed from the plastic bag and rinsed in cold tap water until free of "bleed", dried overnight at room temperature and the electrical resistance of the textiles was then measured.

1.2 Step 2: Contacting of Templated Textile with Polymer Subunits and *in situ* Polymerisation

1.2.1 *In Situ* Polymerisation of Aniline on PMAS Pre-treated Wool Textiles

A sample of the PMAS treated textile of Example 1.1.1 was wound onto a spindle and wet out by soaking at room temperature for 10 min in 1 g/L Lissapol TN450 (ICI, non-ionic surfactant) followed by a distilled water rinse. Aniline was added to distilled water (80 ml) and after stirring for 30 min, the pH was adjusted to pH 1.40 by the drop-wise addition of 10% solution of sulfuric acid and

the final volume was made up to 85 ml.

The spindle was placed in the aniline solution and stirred for 15 min using an overhead stirrer (60 rpm). The *in situ* polymerisation was brought about by the drop-wise addition of a solution of ammonium persulfate in distilled water (15 ml) over a 15 min period to the mixture, which was then left to stir for a further 16 h at room temperature. After the 16 h, the sample was removed, rinsed in cold water and allowed to air dry at room temperature. A significant decrease in electrical resistance from 60 MΩ for the PMAS treated wool to 26 KΩ for the templated textile after the *in situ* polymerisation process was observed.

1.2.2 Variation in PMAS:Aniline Ratio

The method outlined in 1.2.1 above was repeated with modifications to the PMAS:aniline ratio. The results are set out in Table 6. The results show that there is an optimum ratio of PMAS:aniline of approximately 1:2, at a constant aniline:oxidant ratio of 1:0.25.

Table 6:

PMAS:Aniline Ratio	PMAS:Aniline:Oxidant Ratio^	Templated Textile Electrical Resistance
1:1	1:1:0.25	3 MΩ
1:2	1:2:0.5	695 KΩ
1:3	1:3:0.75	1.3 MΩ

^ Polymerisation using constant 1:0.25 aniline: ammonium persulfate ratio in each case.

1.2.3 Variation of Aniline:Oxidant Ratio

The method outlined in 1.2.1 above was repeated with modifications to the aniline:oxidant ratio, where the PMAS:aniline ratio was held constant at 1:2. The results are set out in Table 7. It was found that the range of ratios between 1:0.25 - 1:0.5 afforded the lowest electrical resistance for wool-based textiles.

Table 7:

Aniline:Oxidant Ratio	PMAS:Aniline:Oxidant Ratio	Templated Textile Electrical Resistance
1:0.125	1:2:0.25	1.4+/-0.1 MΩ
1:0.25	1:2:0.5	51.0+/-0.3 KΩ
1:0.5	1:2:1	57.9+/-6 KΩ
1:1	1:2:2	1.10+/-0.2 MΩ

1.2.4 Variation in PMAS Concentration

The method outlined in 1.2.1 above was repeated, with the modification that the PMAS treated textiles used were not those of Example 1.1.1, but those of 1.1.5, having a concentration of PMAS (measured as a percentage based on the mass of the non-conductive textile - that is %omf) of 5%, 10%, 15% and 20%. The results are set out in Table 8. Increasing the PMAS concentration from 5-15% omf results in a decrease in the electrical resistance of templated textiles. However, further increases in PMAS concentration were shown to have only marginal influence.

Table 8:

Initial PMAS Conc. (% omf)	Final % PMAS Exhaustion*	PMAS conc. in Textile (% omf)	Templated Textile Electrical Resistance (KΩ)
5%	99.4	5%	816+/-9
10%	71.1	7.1%	47.3+/-0.8
15%	59.3	8.9%	26.7+/-0.4
20%	46.9	9.4%	30.4 +/-0.4

1.2.5 Variation of Polymerisation Temperature

The method outlined in 1.2.1 above was repeated with modifications to the polymerisation temperature. The results are set out in Table 9. The molecular templated textiles were found to have a lower electrical resistance when the polymerisation was carried out at ambient temperature.

Table 9:

Polymerisation Temperature (°C)	Templated Textile Electrical Resistance (KΩ)
38	394+/-14
23	47.3+/-0.8
2.3	103+/-7

1.2.6 Variation of polymerisation pH

The method outlined in 1.2.1 above was repeated with modifications to the polymerisation pH. The results are set out in Table 10.

Table 10:

Initial pH	Final pH	PMAS Treated Textile Resistance (MΩ)	Templated Textile Electrical Resistance (KΩ)
3.98	2.76	29.7	816+/-9
2.4	2.41	33.8	158+/-6
1.4	1.58	28.7	98+/-8

1.2.7 Variation of Acid Used to Adjust pH of Polymerisation Solution

The method of Example 1.2.1 was repeated with the replacement of the sulphuric acid with hydrochloric acid. The results are set out in Table 11.

Table 11:

Acid	Templated Textile Electrical Resistance (KΩ)
H_2SO_4	47.3+/-0.8
HCL	209+/-2

2 SECOND ALTERNATIVE METHOD FOR FORMING ELECTROCONDUCTIVE TEXTILE

2.1 Contacting of PMAS and Aniline to Wool Textile, and *in situ* Polymerisation of PMAS/Aniline Pretreated Textiles.

A PMAS/aniline mixture was simultaneously applied to a scoured chlorine-Hercosett treated wool knit textile using an Ahiba Texomat Laboratory Dyeing Machine. The wool textile was wound onto a spindle and submerged in the application liquor. The spindle was given constant, steady agitation by the dyeing machine during the course of the application. A standard liquor:goods ratio of 50:1 was used throughout, and the application was made to a 2g sample of wool which had been wet prior to use by soaking at room temperature for 10 minutes in 1g/L Lissapol TN450 (ICI, non-ionic surfactant) followed by a distilled water rinse and a final 10 min soak in acid solution at the desired pH.

The PMAS/aniline mixture solution was adjusted to pH 1.40 by the drop-wise addition of acid (10% w/v H_2SO_4) to the stirred solution. The wool textile was introduced to the application bath at 40°C, heating to the 90°C over 30 minutes, and maintaining this temperature for a further 4 hours. After the completion of the application, the mixture was allowed to cool to room temperature. The *in*

situ polymerisation was brought about by the drop-wise addition of a solution of ammonium persulfate in distilled water (15 ml) over a 15 min period to the mixture, which was then left to stir for a further 16 h at room temperature. After the completion of the application, the textile sample was removed from the application liquor and rinsed in cold tap water until no signs of "bleed" were evident. Excess water was removed and the sample was air-dried at room temperature. The wool textiles prepared using this method had electrical resistances in the range from 30 KΩ to 250 KΩ.

3 THIRD ALTERNATIVE METHOD FOR FORMING ELECTROCONDUCTIVE TEXTILE

3.1 Step 1: Synthesis of Preformed Templated Polymers

A series of templated polymers were prepared in the presence of 0.02M PMAS using different concentrations of aniline, as set out in Table 5. Aniline was added to an aqueous solution of PMAS and the resulting solution's pH of about 5.4 was adjusted to pH 2 by the addition of HCl (conc.). The required amount of ammonium persulfate solution to facilitate the polymerisation (set out in Table 5) was added drop-wise at such a rate as to maintain the reaction temperature below 24°C. The thick polymer solution obtained was stirred overnight and then dialysed by using 12kD dialysis tubing. After dialysis the polymer solution was stirred and heated to about 50°C to concentrate the polymer, and then left to dry by evaporation in a fume hood. The conductivities of pressed pellets of the templated polymers were then measured, and the results are set out in Table 12. Conductivities of

pressed pellets as high as 6.8 S/cm were obtained.

Table 12:

Molecular Templating Concentrations	Oxidant Concentration $(NH_4)_2S_2O_8$	Conductivity S/cm	pH
PMAS + Aniline (0.02M + 0.02M)	0.02M	0.05	2
PMAS + Aniline (0.02M + 0.06M)	0.06M	6.8	2
PMAS + Aniline (0.02M + 0.08M)	0.08M	5.1	1.9
PMAS + Aniline (0.02M + 0.05M)	0.055M	1.2	2
PMAS + Aniline (0.02M + 0.037M)	0.02M	1.0	2.1

3.2 Step 2: Application of Preformed Molecular Template to Non-conductive Textile

The PMAS/PAn (polyaniline) preformed template and conductive polymer of Example 3.1 containing PMAS:Aniline:oxidant ratio 0.02M:0.06M:0.06M was applied to scoured chlorine-Hercosett treated wool knit textile using an Ahiba Texomat Laboratory Dyeing Machine. The wool textile was wound onto a spindle and submerged in the application liquor, and the spindle was given constant, steady agitation by the dyeing machine during the course of the application. A standard liquor:goods ratio of 50:1 was used throughout this example, and the application was made to a 2g sample of textile which had been wet prior to use by soaking at room temperature for 10 minutes in 1g/L Lissapol TN450 (ICI, non-ionic surfactant) followed by a distilled water rinse and a final 10 min soak in acid solution at the desired pH.

The PMAS/PAn template solution was adjusted to pH 1.40 by the drop-wise addition of acid (10% w/v H_2SO_4) to

the stirred solution. The wool textile was introduced to the application bath at 40°C, heated to 90°C over 30 minutes, and this temperature maintained for a further 4 hours. After the completion of the application, the textile sample was removed from the application liquor and rinsed in cold tap water until no signs of 'bleed" were evident. Excess water was removed and the sample was air-dried at room temperature. The products were found to have electrical resistance values in the range of 1-10 MΩ.

4 Use of Other Macromolecular Templates and Conductive Polymers.

Experiments using Method I (see Figure 1) where polystyrene sulfonate (PSS^-) (MWt 70,000) is the macromolecular template showed that this polyelectrolyte can also assist in the incorporation of polyaniline into wool/nylon/Lycra. Further experiments also with Method I showed that by using PMAS as a template, polypyrrole incorporation into wool/nylon/Lycra can be facilitated.

4.1 Templating of Polypyrrole onto PMAS-treated Wool Fabric

The PMAS/polypyrrole templated was formed by application of method I to PMAS treated chlorine-Hercosett wool prepared by the procedure of 1.1.1. (Table 13)

Table 13:

PMAS:Pyrrole:oxidant	Templated Textile Electrical Resistance (KΩ)
1:2:2	17.3+/-0.1
1:4:4	1.87+/-0.03

5 PHYSICAL CHARACTERISATION OF MOLECULAR TEMPLATED

TEXTILES

5.1 UV-VIS Spectral Evidence of Formation of Molecular Template

The UV-VIS spectra using 1,2-dichlorobenzene of wool textiles relating to the various stages of the *in situ* templating process are shown in Figure 2. The increased adsorption of higher wavelengths of the templated systems is indicative of the formation of the PMAS/PAn molecular template. The figure also demonstrates that the characteristic PMAS band at 474 nm has decreased and absorption around 800 nm typical of polyaniline in the expanded coil form has increased.

5.2 Scotch Tape Test

Each of the electroconductive textile products produced in the Examples outlined above was subjected to the standard scotch tape test to assess bonding of the conductive polymer to the non-conductive textile. Briefly, the test involves adhering commercially available scotch sticking tape to the treated textile, peeling the tape from the treated textile and visually determining whether any polymer has been removed with the tape. All systems evaluated passed the test with no sign of removal of the ICP (see Table 14).

Table 14:

Fabric	Scotch tape test
PMAS Wool/nylon/Lycra	No removal of polymer
PMAS/PPy Wool/nylon/Lycra	No removal of polymer
PMAS/PAn Wool/nylon/Lycra	No removal of polymer
PPy Wool/nylon/Lycra	No removal of polymer
Preformed PMAS/PAn Wool/nylon/Lycra	No removal of polymer

5.3 Effect of washing on conducting polymer treated textiles

The PMAS/PAn electroconductive textile prepared by Method I (as represented in Figure 1) was subjected to a standard wash procedure. The test used was a Modified Woolmark Test Method 31, Washing of wool textile products: Standard 7A wash cycle, and was performed in a Wascator FOM 71 MP washing machine. The sample size was 100x100 mm. The results of the washing treatment were compared to a polyaniline and polypyrrole treated textile of the prior art which did not contain the macromolecular template. The results are set out in Table 15.

Table 15 also details the results of an acid treatment conducted on the same textiles. After treatment of the washed samples with aqueous sulfuric acid (pH 1.4), the PMAS/PAn treated textile shows a significant decrease in electrical resistance whereas the polypyyrole system has increase in electrical resistance. The polyaniline sample shows no evidence of a decrease in its electrical resistance after the acid treatment.

Table 15:

	Polyaniline (PAn)	PMAS	PMAS/PAn	Polypyrrole (PPY)
Starting textile	2.1 M Ohm	77 M Ohm	130 KOhm	4.2 K Ohm
Washed textile*	>1.2 G Ohm	143 M Ohm	504 KOhm	10.3 K Ohm
Acid wash	>1.2 G Ohm	155 M Ohm	304 K Ohm	124 KOhm

* Modified Woolmark Test Method 31, Washing of wool textile products: Standard 7A wash cycle. Sample size was 100x100 mm

5.4 Effect of rubbing on conducting polymer treated textiles

The colourfastness to dry rubbing of PMAS/PAn electroconductive textile prepared by Method I (as represented in Figure 1) was determined in accordance with Australian Standard 2001.4.3 - Determination of Colourfastness to Rubbing, using an Atlas Crockmeter. This test involves the dry rubbing of treated textiles using a standard undyed cotton textile (1M ISO Cotton Rubbing Fabric, supplied by Australian Wool Testing Authority). In addition to the standard 10 rubs required for the test method, extra rubs were performed. This test showed that the PMAS/PAn molecular templated textile had less removal of conducting polymer from the textile due to abrasion than the polyaniline and polypyrrole treated textiles. The alternative molecular templated textile, PMAS/PPY had improved rubfastness compared to the textile treated with only polypyrrole.

Table 16:

	Polyaniline (PAn)	PMAS	PMAS/PAn	PMAS/PPY	Polypyrrole (PPY)
Perpendicular					
10 rubs	4	4	4	4	3-4
20 rubs	3-4	3-4	3-4	3-4	3
30 rubs	3	3-4	3-4	3-4	2-3
40 rubs	3	3-4	3	3-4	2-3
Parallel					
10 rubs	3-4	4-5	4	4	3-4
20 rubs	3	4	3-4	4	3
30 rubs	3	3-4	3-4	3	3
40 rubs	3	3-4	3-4	3-4	3

Grey scale ratings 5 to 1 white through to grey. A rating of 5 indicates that no polymer is abraded onto the white cotton test fabric.

6 *IN SITU* TEMPLATED COATINGS AS WEARABLE TEXTILE STRAIN GAUGES.

The effect on electrical resistance due to the straining of a range of PMAS/PAn molecular templated wool/composite textiles was determined. The dynamic calibrations at frequencies up to 3 Hz and over a range of 10-70% strain showed that the results compared well with those obtained using *in situ* coated polypyrrole on wool/Lycra. Unlike the polypyrrole-coated materials, minimal change in electrical resistance responses was observed over a three-week period for the PMAS/PAn electroconductive textiles.

It will be understood to persons skilled in the art of the invention that many modifications may be made without departing from the spirit and scope of the invention.

Figure 1

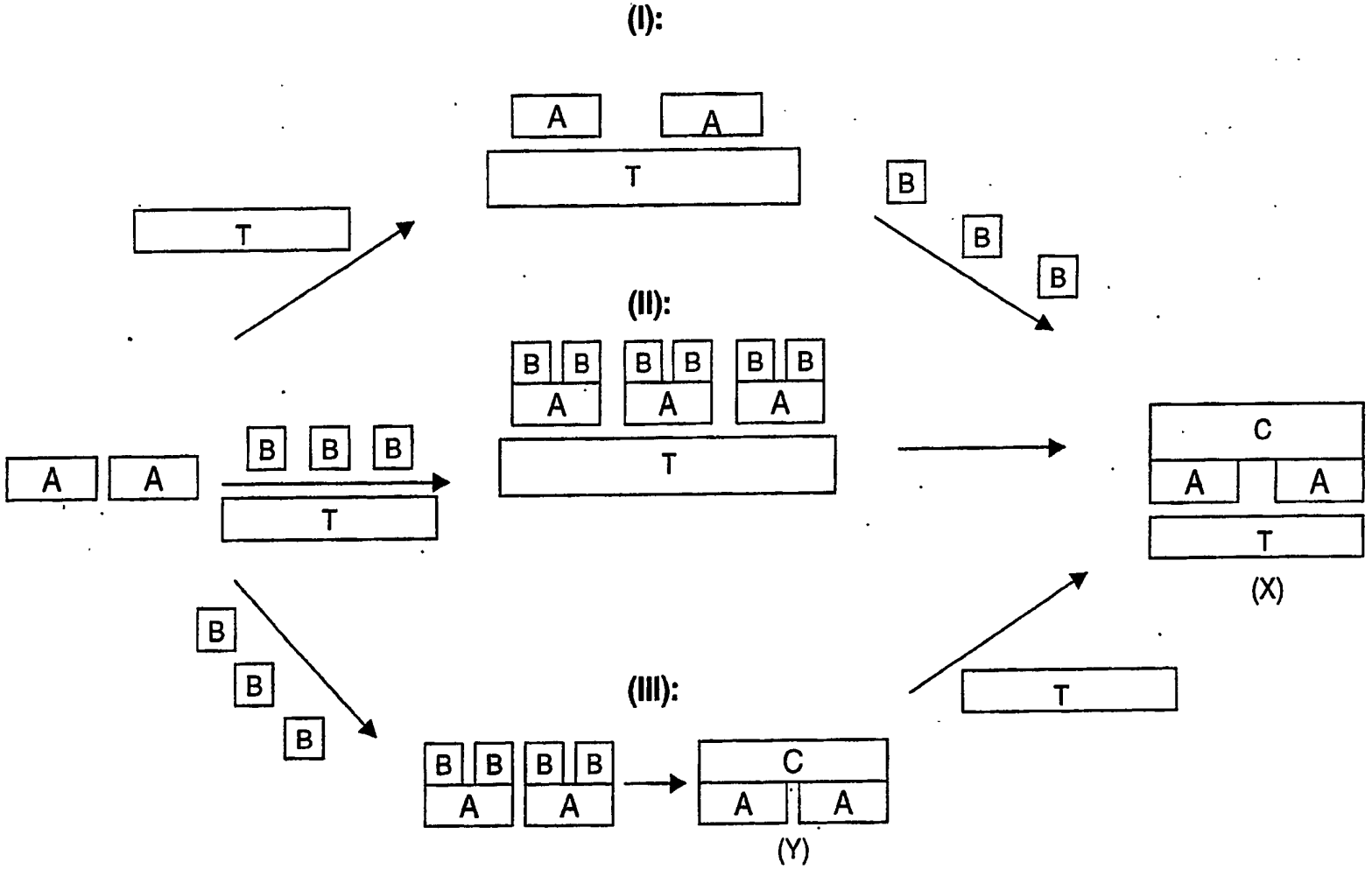
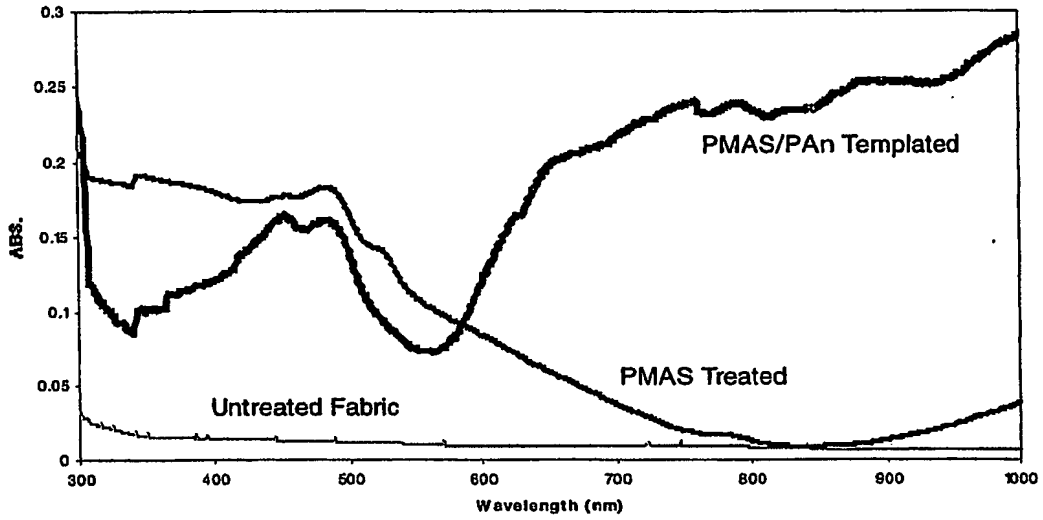


Figure 2:


0.3
0.25
0.2
0.15
0.1
0.05
0
ABS.
300
400
500
600
700
800
900
1000
Wavelength (nm)
PMAS/PAn Templated
PMAS Treated
Untreated Fabric

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